Combustion Instability Studies with Plastic Propellent

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The effect of compositional changes on the stability of combustion of plastic propellent, based upon ammonium perchlorate and polyisobutene, is investigated using a 2-in.-diam T burner for the frequencies 0.7–4.0 kHz at 1000 psig. Oxidizer particle size can have a pronounced effect both on the acoustic response and on the maximum pressure amplitude which can be sustained in the T burner, whereas changes in the oxidizer-fuel ratio have little effect. Titanium dioxide, usually added to plastic propellent to stabilize combustion, is shown to have a dual effect: the acoustic response is reduced and the gas phase particle damping is promoted. Finally, the effect of lithium fluoride and copper chromate on combustion instability is examined. An inverse correlation, which is frequency dependent, is observed between propellent burning rate and both the acoustic response and the maximum pressure amplitude sustained in the T burner.

Nomenclature

a = constant in burning rate expression $r = aP^n$
b = radius of burner tube
c = velocity of sound
f = frequency
n = pressure exponent
P = pressure
P_A = acoustic pressure amplitude
r = linear burning rate
S_0 = specific surface area expressed as cm^2/cm^3 or cm^{-1}
T_g = burner tube temperature when α_g measured
T_d = burner tube temperature when α_d measured
α_g = logarithmic rate of growth of pressure oscillations
α_d = logarithmic rate of decay of pressure oscillations
ϵ = fractional perturbation of pressure
η = viscosity of gas in burner tube
ρ_{gas} = density of gas in burner tube
ρ_{solid} = density of solid propellent
μ = fractional perturbation of mass flow rate associated with ϵ

Introduction

Although much progress has been made in recent years towards the understanding of the factors contributing to combustion instability, this understanding is still far from comprehensive. For instance, it is extremely difficult to predict the effect of a compositional change in a propellent on the stability of its combustion. It is therefore still necessary to test experimentally the tendency to instability of each propellent system and each additive.

This paper gives results which have been obtained at the Rocket Propulsion Establishment, Westcott, for the British made plastic propellent which is based on ammonium perchlorate (AP) as oxidizer and polyisobutene as fuel. Titanium dioxide (TiO_2) is frequently added to such propellants to reduce the tendency for unstable combustion. The effects of varying the proportion of TiO_2 added and also of variations in the AP particle size both in the presence and absence of TiO_2 have been studied. Since considerable interest has recently been shown in oxygen balanced propellents, the effects of changes in the propellent oxidizer/fuel ratio have also been investigated. Finally, the effect of two ballistic modifiers, lithium fluoride and copper chromate has been studied.

Experimental

The T burner used at the Rocket Propulsion Establishment is described in detail in an earlier paper[1] and is similar to that devised by Price and his group[2,3] at the Naval Weapons Center, China Lake. It consists basically of a tube 50.8 mm internal diameter and 25.4 mm wall thickness, closed at both ends, in which the gas oscillates in the fundamental longitudinal mode. The burner tube length can be varied so that frequencies in the range 0.7–4.0 kHz may be studied. An orifice of 12.7 mm diam, located centrally in the burner tube is connected to a 0.11 m^3 (4 cu ft) surge tank. This prevents any appreciable change in the mean pressure during burning and since the connection is at the center of the burner tube, i.e., at a pressure node, acoustic losses are minimized. The system is pressurized with nitrogen to a pressure of 6.894 MN/m^2 (1000 psig) before firing and the propellent is ignited by small cartons containing 0.4 g of a standard pyrotechnic composition. The pressure in the burner tube is measured by quartz piezoelectric transducers (Kistler Instrument Corp. or Vibrometer Corp.) and recorded photographically from a four channel oscilloscope. The pressure could be measured either adjacent to the propellent surface or behind the propellent surface. It was confirmed that both these locations gave the same results. The amplitude of the oscillatory component of the pressure could be readily measured with values as low as 6.9 kN/m^2 (1 psi).

The propellent charges are prepared for use by first coating the T burner end caps with Pliobond 20 (Goodyear, Great Britain) and then pressing an accurately weighed amount of propellent, 33.4 g, into each end cap. This resulted in each propellent disk being 10.2 mm (0.4 in.) thick. In all the firings reported in this paper two propellent disks were used for each firing and were mounted symmetrically at each end of the burner.

The compositions and some of the ballistic properties of the propellents used for this work are given in Table 1.

Results

All the firings reported here were carried out at a mean pressure of 6.894 MN/m^2 (1000 psig). This pressure was chosen as being representative of most solid propellent croket motor firings.

Presented as Paper 69-478 at the AIAA 5th Propulsion Joint Specialist Conference, U.S. Air Force Academy, Colorado, June 9–13, 1969; submitted June 19, 1969; revision received June 26, 1970. The author would like to thank G. J. Spickernell of the ERDE, Waltham Abbey, Essex, England, for his assistance in preparing the special propellent samples, J. Gittins and the staff of R Site for the care they took with the firings and also G. S. Pearson for his constructive suggestions and interest.

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Table 1 Compositions and some ballistic properties of the propellents

Propellent	AP, %	S_0 AP, cm^{-1}	USB2,[a] %	TiO_2,[b] %	LiF,[c] %	$CuCrO_4$,[d] %	Burning rate at 6.894 MN/m^2, mm/sec	Specific impulse, sec
A	84	1930	12	4	0	0	26.0	...
B	86	1930	12	2	0	0	25.8	...
C	87	1930	12	1	0	0	23.9	...
E	88	9100	12	0	0	0	27.3	...
F	88	400	12	0	0	0	14.2	...
I	87	400	12	1	0	0	18.3	...
J	87	9100	12	1	0	0	32.5	...
Y	87	1930	12	0	1	0	11.6	...
S	87	1930	12	0	0	1	29.8	...
T	86	1930	12	0	0	2	35.6	...
N	86	1930	14	0	0	0	16.1	243.0
D	88	1930	12	0	0	0	17.4	248.3
L	89.5	1930	10.5	0	0	0	20.8	251.3
M	90.5	1930	9.5	0	0	0	22.4	252.0
...[e]	90.75	...	9.25	0	0	0	...	251.6

[a] USB2 consists of 90% polyisobutene [$(CH_2)_n$] and 10% S101 ($C_{1.0}H_{1.873}O_{0.173}$).
[b] S_0TiO_2 = 60,000 cm^{-1}.
[c] S_0LiF = 63,700 cm^{-1}.
[d] S_0CuCrO_4 = 40,000 cm^{-1}.
[e] This propellent contains the theoretical stoichiometric ratio.

For each propellent the logarithmic rates of growth and decay of the pressure oscillations were plotted against frequency. Mean growth and decay constants were read off at a series of set frequencies, and the acoustic response was evaluated at these set frequencies using the standard T burner equation

$$Re(\mu/\epsilon) = (P/4r\rho_{\text{solid}}fc)(\alpha_g - \alpha_d) \quad (1)$$

Since the decay constants were measured while the gas in the burner tube was cooling it was necessary to correct them for the effect of this lower temperature (T_d) before application of Eq. 1. The decay constants were corrected to the gas temperature (T_g) appropriate to the measurement of the growth constants in the following way. If it is assumed that the majority of the acoustic attenuation is associated with viscous resistance offered to the fluid motion at the walls of the burner tube, then the decay constant is given by,[4]

$$\alpha_d = (\pi f\eta/\rho_{\text{gas}})^{1/2}/b \quad (2)$$

where b is the burner tube radius. When the allowances for the effect of temperature on η and ρ_{gas} are made, the decay constants are related by

$$\alpha_d(\text{at } T_g) = \alpha_d(\text{at } T_d)(T_g/T_d)^{0.75}$$

The over-all effect of this correction on the final value of $Re(\mu/\epsilon)$ is small and in most cases less than 5%.

In the majority of T burner firings a steady maximum pressure amplitude was reached when the acoustic losses and gains for the system were balanced. This is a second useful quantity for the comparison of the combustion stability of propellents and it is therefore plotted against frequency for each propellent.

Discussion

1. Effect of Variation of Ammonium Perchlorate Particle Size

The propellents used for this section of the research are split into two groups in which the oxidizer particle size was varied: 1) propellents F, D, and E containing 88% AP and 12% USB2 (90% polyisobutene + 10% S101 wetting agent), and 2) propellents I, C, J containing 87% AP, 12% USB2 and 1% TiO_2. There is a slight change in the oxidizer/fuel ratio between these two groups of propellents but other experiments (Sec. 3) have shown that this small change has little effect on the acoustic response or other associated property.

Table 1 shows that, as the oxidizer particle size is reduced, the linear burning rate of the propellents as measured under steady-state conditions increases. This is observed for both groups of propellents and the percentage change in burning rate is similar in each group for the same alteration in the oxidizer particle size.

The tendency of the propellents to burn unstably is shown in Fig. 1 in which, as the frequency increases, the real parts of the acoustic response for the three propellents F, D, and E all tend towards the same value (~1.0), indicating that at high frequencies $Re(\mu/\epsilon)$ is independent of oxidizer particle size. At the lower frequencies, $Re(\mu/\epsilon)$ decreases with a decrease in the oxidizer particle size. Now, as the pressure exponent n in the burning rate expression

$$r = aP^n \quad (3)$$

is similar (0.5–0.7) for all the propellents considered here and because at zero frequency μ/ϵ approaches n, the lines on Fig. 1 must again converge at frequencies below 0.7 kHz. There is thus only a limited frequency region where μ/ϵ is dependent upon particle size.

Similar work has been carried out at the N.W.C. by Price and his group[3,5] who varied the AP particle size in a pro-

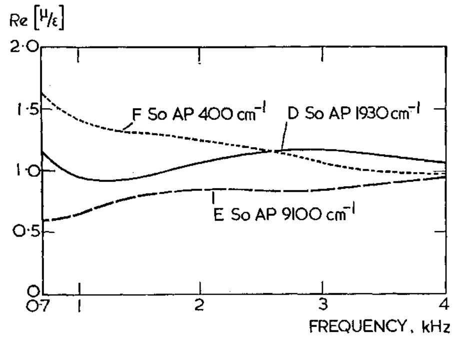

Fig. 1 Effect of oxidizer particle size on $Re(\mu/\epsilon)$ for propellents containing 0% TiO_2 (propellents F,D,E).

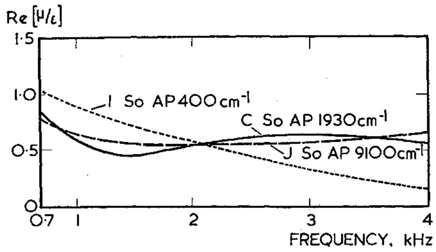

Fig. 2 Effect of oxidizer particle size on $Re(\mu/\epsilon)$ for propellents containing 1% TiO_2 (propellents I,C,J).

pellent based upon polybutyl acrylic acid (PBAA) as the fuel. At a pressure of 1.379 MN/m^2 (200 psi) it was found that changing the particle size of the oxidizer simply changed the burning rate of the propellent. This was based on plots of $Re(\mu/\epsilon)$ against f/r^2 which was supposed to remove any burning rate dependence.

Consideration of the propellents containing 1% TiO_2, I, C, and J (Fig. 2) shows that the acoustic response is reduced in each case compared to the propellents containing no TiO_2 but the reduction is most marked for propellent I. It can be seen that for both propellents with coarse oxidizer (I, F) the acoustic response decreases steadily as the frequency increases, whereas with all the other propellents used in the work the acoustic response has been practically independent of frequency. This indicates an increasing tendency to stability at higher frequencies for propellents containing coarse oxidizer.

2. Effect of Addition of TiO_2 to Plastic Propellent

2.1 Addition of 1% TiO_2 to propellents with different AP particle size

When Figs. 1 and 2 are compared it is seen that 1% TiO_2 reduces the acoustic response of each propellent, the effect being greatest when coarse oxidizer is used and at high frequencies. The effect on the maximum pressure-amplitude is shown in Figs. 3–5, from which the following results are evident: a) Fine oxidizer—1% TiO_2 reduces the maximum pressure-amplitude by a factor of ~2.5 (Fig. 3); b) Medium oxidizer—1% TiO_2 reduces the maximum pressure-amplitude by a factor of ~2.5 at high frequencies and by a factor of 10 at low frequencies (Fig. 4); c) Coarse oxidizer—1% TiO_2 reduces the maximum pressure-amplitude by a factor of 100–150 over the whole frequency range (Fig. 5).

It should be noted that with the propellents containing coarse oxidizer, the maximum pressure-amplitude decreases with increase of frequency whereas with the propellents containing fine oxidizer it increases with increase of frequency.

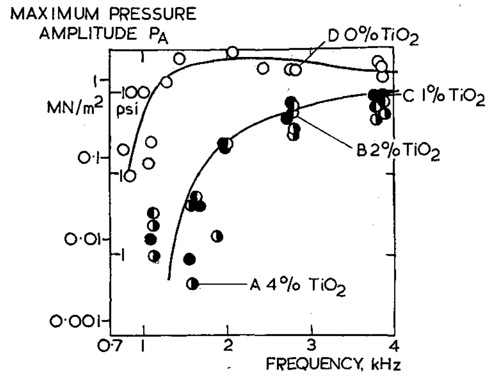

Fig. 4 Effect of 1, 2, and 4% TiO_2 in propellent with medium grade oxidizer on maximum pressure amplitude (propellents D,C,B,A).

2.2 Addition of up to 4% TiO_2 to propellent containing medium AP

The four propellents (A, B, C, and D) used for this section of the work contained a constant 12% USB2 and 4, 2, 1, and 0% TiO_2, respectively. Their burning rates are given in Table 1. Addition of 1% TiO_2 to propellent D causes an increase in the burning rate of 37% whereas the addition of a further 1% TiO_2 increases the burning rate only 8%, i.e., an increase of 45% over D. An increase in the TiO_2 content from 2 to 4% increases the burning rate by only a further 1%. Thus, under steady-state conditions, an addition of 1% TiO_2 has a marked effect on the burning rate, whereas further additions have only slight effects. The mechanism by which TiO_2 influences the steady-state burning rate is uncertain at present; however, it is known to have little effect upon the decomposition temperature of AP.[6]

The real parts of the acoustic response $Re(\mu/\epsilon)$, for all three propellents containing TiO_2 are similar and significantly less than for the propellent with no TiO_2. TiO_2 has, therefore, a marked effect on the change in mass burning rate for given perturbation in pressure and, as in its effect on the steady state combustion, the change is similar for 1, 2, or 4% of TiO_2.

A lower maximum pressure-amplitude was supported in the T burner for all the propellents containing TiO_2 than for the propellent without TiO_2 (Fig. 4). The propellent containing 4% TiO_2 sustained the lowest pressure-amplitude but the increased effect of 4% as compared to 1% was most noticeable at the higher frequencies. At the lower frequencies where the reduction in pressure-amplitude was the greatest, the effect was similar regardless of whether 1, 2, or 4% of TiO_2 was added to the propellent. A similar trend was evident when the rates of decay of the pressure oscillations in the T burner were plotted against frequency. Both these effects are most

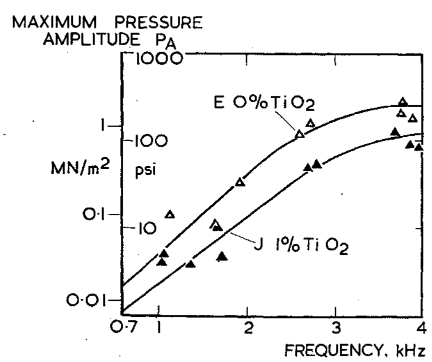

Fig. 3 Effect of 1% TiO_2 in propellent with fine oxidizer on maximum pressure amplitude (propellents E,J).

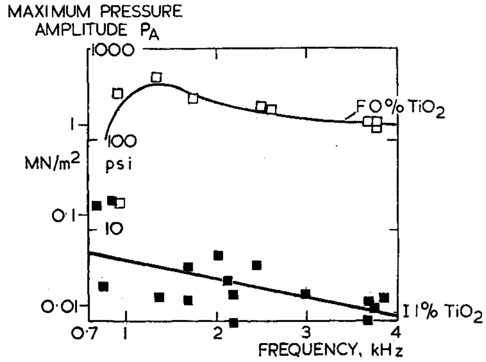

Fig. 5 Effect of 1% TiO_2 in propellent with coarse oxidizer on maximum pressure amplitude (propellents F,I).

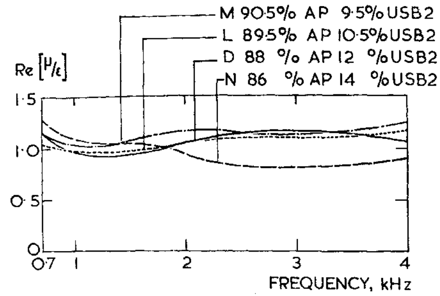

Fig. 6 Effect of varying the oxidizer/fuel ratio on $Re(\mu/\epsilon)$ (propellents N,D,L,M).

likely caused by particulate damping by the TiO_2 in the gas phase.

3. Effect of Variation of the Oxidizer/Fuel Ratio of the Propellent

The effect on the acoustic response of varying the AP/USB2 ratio is shown in Fig. 6. The change in oxidizer/fuel ratio is from 6.1 to 9.5 (stoichiometric is at 9.81) but the change in acoustic response is slight. Propellent M which is close to the stoichiometric mixture does have a marginally higher acoustic response, but propellents D, L, and M are all similar. Propellent N, which is the most fuel-rich, shows the lowest acoustic response at the higher frequencies. This is probably due to the energy content of propellent N being lower than for the other propellents as shown by their specific impulse given in Table 1. A similar result is obtained when the maximum pressure amplitudes reached in the T burner are plotted against frequency.

Rice,[7] who has carried out similar experiments on an AP/PBAA propellent system, found that the most fuel-rich propellent had the highest acoustic response. This is in direct contradiction to the results found here. The most likely cause for the different findings is that Rice's experiments were carried out at a mean pressure of 1.379 MN/m^2 (200 psi), whereas the present firings were all at 6.894 MN/m^2 (1000 psi) and a different flame structure is probably present.

4. Effect of Ballistic Modifiers

Copper chromate or lithium fluoride are occasionally added to plastic propellent to increase, or decrease respectively, the mean solid propellent burning rate. Figure 7 illustrates the effect on the maximum pressure amplitude of 1 or 2% copper chromate or 1% lithium fluoride.

Lithium fluoride is destabilizing whereas copper chromate is mildly stabilizing. The effect of copper chromate is practically independent of whether 1 or 2% was added to the propellent. The additives did not appear to modify the decay constants for the pressure oscillations, suggesting that the effect on stability was located in the combustion phase.

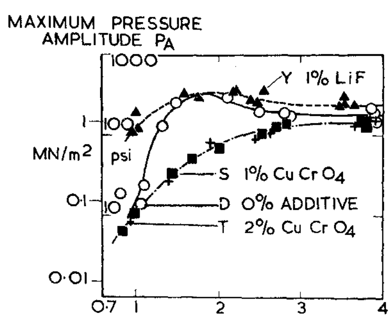

Fig. 7 Effect of 1% lithium fluoride and 1 and 2% copper chromate on maximum pressure amplitude.

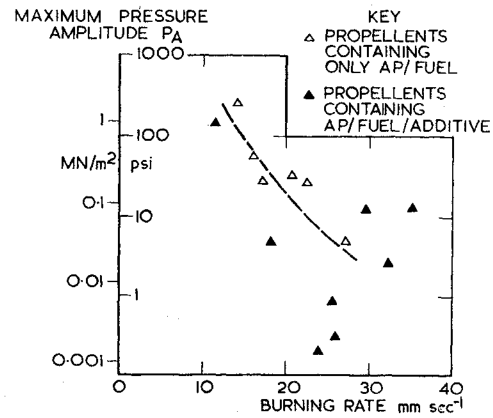

Fig. 8 Maximum pressure amplitude at a frequency of 1.0 kHz as a function of propellent burning rate.

Comparable experiments have been carried out by Horton and Rice[8] on the influence of copper chromite on an AP/PBAA propellent system. Note the use of copper chromite as a burning rate catalyst in American propellents compared to copper chromate in British propellents. At a pressure of 1.379 Mn/m^2 (200 psi) the copper chromite reduced the acoustic response over the greater part of the frequency range studied. However, when coarse oxidizer (80 μ = S_0 750 cm^{-1}) was used, the acoustic response was only less than that for the propellent with no additive when the frequency was below 3.5 kHz; with fine oxidizer (15 μ = S_0 4000 cm^{-1}) the frequency had to be less than 6 kHz to obtain the same effect.

5. Correlation between Mean Burning Rate and Instability

The maximum pressure amplitude which each propellant can sustain in the T burner is shown as a function of the mean burning rate of the propellent in Fig. 8 for the frequency 1 kHz. An approximate correlation is evident.

As the burning rate of the propellent is decreased, either by use of a ballistic modifier, by changing the oxidizer/fuel ratio or the oxidizer particle size the maximum pressure amplitude sustained by the propellent is increased. Figure 9 shows a similar trend when the acoustic response is plotted against burning rate.

To determine if the maximum pressure amplitude is an independent quantity and therefore valid as a criterion for stability, the maximum pressure amplitude is shown against the acoustic response for each propellent at two frequencies, 1.0 and 3.5 kHz, in Fig. 10. It is apparent that the maximum pressure amplitude attained in the T burner is approxi-

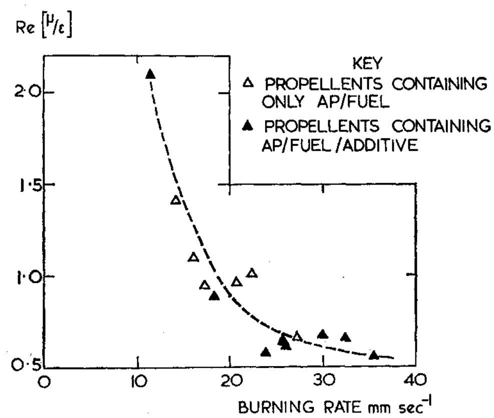

Fig. 9 Acoustic response at a frequency of 1.0 kHz as a function of propellent burning rate.

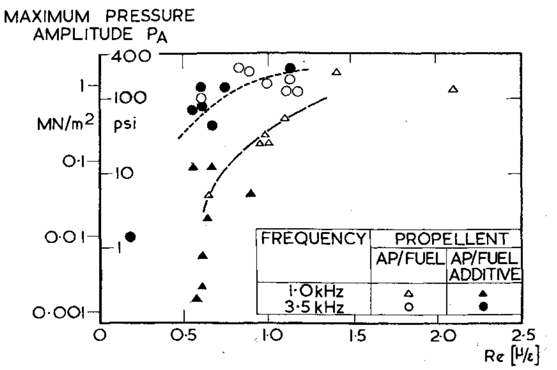

Fig. 10 Maximum pressure amplitude as a function of acoustic response.

mately correlated with the acoustic response, particularly at the lower frequency of 1 kHz. As this correlation is only fair, it shows that, as expected, effects other than the acoustic gain at the burning surface, such as gas phase particle damping, play an important part in determining the over-all limiting pressure amplitude which a propellent can sustain. Thus the maximum pressure amplitude does provide another useful piece of data from the T burner. However, the small range of propellents examined here needs to be enlarged considerably before firmer conclusions can be drawn linking burning rate, acoustic response and maximum pressure amplitude.

A possible explanation for the greater tendency to instability of the slower burning propellents is because of the flame zone being located further away from the propellent surface. Thus a larger amplitude of oscillation of the flame position can be sustained before interference occurs with the solid surface.

Conclusions

1) The stability of burning of a solid propellent is affected by a change in the AP particle size:

a) In the absence of TiO_2, at high frequencies (4 kHz) the acoustic response is independent of AP particle size, but at the lower frequencies (1 kHz) the acoustic response is greatest for the propellent containing coarse oxidizer.

b) The acoustic response is reduced for each propellent in the presence of 1% TiO_2 but the effect is greatest when the propellent contains coarse oxidizer at the higher frequencies.

2) Titanium dioxide promotes stable burning in plastic propellents by two major routes:

a) In the gas phase it promotes acoustic damping by means of the fine suspended solid particulate matter. The amount of gas phase particulate damping is proportional to the percentage of TiO_2 added to the propellent. This proportionality is most noticeable at the high frequencies (4.0 kHz) and the effectiveness of the damping is most evident at lower frequencies (1.5 kHz).

b) Titanium dioxide also exerts an influence on the combustion zone and additions of 1, 2, or 4% titanium dioxide to the standard medium grade oxidizer propellent all lower the acoustic response by a similar amount, ~50%, over the whole frequency range. However, at higher frequencies 1% TiO_2 has a much greater stabilizing influence on the combustion of the propellent containing coarse oxidizer.

3) The variation of the oxidizer/fuel ratio over a comparatively wide range has little effect on the stability of burning of plastic propellents. The results show that as the energy level of the propellent is reduced so is its tendency to instability but the effect is small.

4) From a study of the above propellents and others containing lithium fluoride and copper chromate an approximate correlation has been observed between propellent burning rate, acoustic response, and the maximum pressure-amplitude which the propellent can sustain in the T burner. A lower burning rate propellent is more likely to have a higher acoustic response and sustain a higher amplitude of pressure oscillations than a faster burning propellent. This is much more evident at a frequency of 1 kHz than 3.5 kHz. However there are important secondary effects, e.g., gas phase particle damping which can further limit the amplitude of the pressure oscillations. It is suggested that slow burning propellents show a greater tendency to intermediate frequency instability than faster burning propellents since the flame zone is located further away from the solid surface. Hence the flame can sustain a larger amplitude of oscillation in its position before interference occurs with the solid surface.

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